INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2015) 1–15

Available online at www.sciencedirect.com

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journal homepage: www.elsevier.com/locate/he

Thermocatalytic CO_2 hydrogenation for methanol and ethanol production: Process improvements

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ARTICLE INFO

Article history:
Received 20 July 2015
Received in revised form
25 November 2015
Accepted 1 December 2015
Available online xxx

Keywords:
Carbon utilization
Water electrolysis
Process modeling
Economic assessment
Methanol
Ethanol

ABSTRACT

This study investigates various design aspects for the valorization of industrially captured CO_2 towards methanol and/or ethanol. In the framework of the CO_2 conversion unit, two novel concepts are examined aiming to the improvement of the process performance, one for methanol and another for ethanol production. For the methanol case ($CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$), a new scheme of employing a membrane reactor with high selectivity either in methanol permeation (organophilic) or in water permeation (hydrophilic) is explored via process simulation. The methanol extraction has a beneficial effect on the methanol yield and requires a more compact sized reactor. In ethanol case ($2CO_2 + 6H_2 \rightarrow C_2H_5OH + 3H_2O$), a new process configuration through the intermediate DME (di-methyl ether) synthesis is presented and compared to the conventional method based on CO_2 conversion to CO in a reverse water gas shift (rWGS) reactor followed by the mixed alcohol synthesis reactor. The novel synthesis route via DME has a higher efficiency (total energy efficiency: 70.3% on LHV basis whereas the corresponding efficiency of the conventional scheme is 63.2%) because of lower heat and power demands for its effective operation. From the economic analysis, it is shown that the novel ethanol plant results to lower ethanol production cost than the conventional one through the rWGS by 18% but the high cost for H_2 production through water electrolysis keeps it far for competitive levels.

Introduction

An option for the drastic mitigation of CO_2 emissions, alternative to the Carbon Capture and Storage concept, is to transform it into valuable compounds, like fuel and chemicals, namely as 'the CO_2 capture and utilization (CCU) concept'. The majority of CO_2 use in industry is for urea production, which accounts for more than half of the global annual usage [1]. Alternatively, CO_2 is utilized also physically in various applications such as refrigerant medium, in fire extinguishers and in the petroleum and NG industry for Enhanced Oil Recovery (EOR) and Enhanced Gas Recovery (EGR), respectively [2,3].

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http://dx.doi.org/10.1016/j.ijhydene.2015.12.001

In order the CCU concept to have effective impact on the drastic reduction of the CO_2 emissions, the quantities of end-products derived from CO_2 transformation should cover the market demand. The selection of the final products should be correlated to global demands and consumptions of them. Thus, this study focuses on synthesis of alcohols that can be used as alternative fuels in the transportation sector. The method for CO_2 transformation that is examined in this study is the catalytic hydrogenation, which is considered the most mature and old technology in this field.

There are three routes for non-fossil derived hydrogen production: water electrolysis, biomass conversion and solar conversion [4,5]. In the present study, the hydrogen is considered to be derived from electrolysis, since this is the most mature and well-established technology even in industrial scale [6] and also it is not relied on carbon-contained source like biomass. Electrolysis is based on the water splitting into H_2 and O_2, the energy for this reaction is given in the form of electricity derived from Renewable Energy Source (RES) i.e. photovoltaic panels (PV), wind farms hydropower and geothermal plants. Since the H_2/CO_2 ratio for CO_2 hydrogenation towards hydrocarbons synthesis should be four (4) for methane and three (3) for methanol synthesis, the required amounts of hydrogen are very large.

Methanol is one of the most valuable chemicals with a series of uses either as fuel or as block for the synthesis of other chemicals. The last years there is an interest in the production of methanol from CO_2, based on the so called "Power-to-Fuel" concept. In Iceland, a demonstration plant with annual methanol production 4000 tons is operating since 2011 and a larger plant with capacity 40,000 t/y is be constructed by Carbon Recycling International (CRI) [7]. Blue Fuel Energy will built a methanol plant with production capacity 400,000 t/y, powered by renewable electricity in Canada [8].

Apart from methanol, ethanol is gaining the interest the last decades not only as an alternative fuel [9,10] but also a valuable chemical block for numerous products synthesis [11]. In order the CCU concept to become the most appropriate option for CO_2 mitigation in a global scale, the synthesis of several chemical products should be included in a generalized road map. Ethanol is considered as a perfect additive into petrol, contributing to the increase of octane number and the reduction of CO and PM emissions. Furthermore, ethanol has an important advantage over methanol for application as transportation fuel because it is less toxic and dangerous, permitting higher blending ratios with conventional gasoline [12,13]. However, the alternative ethanol fuel is bio-based and is mainly produced from sugar/starch crops through fermentation. On the other hand, few studies [14–16] that have investigated the technical and economic prospects for CO_2 derived ethanol synthesis.

The scope of this study is the investigation of new process schemes for the valorization of CO_2 towards the production of methanol and ethanol. In the methanol case, the use of membrane catalytic reactor for the fuel synthesis is examined whereas in the ethanol case, a novel concept is presented that based on the use of DME as intermediate product. The produced alcohols (methanol, ethanol and DME) can be used either as transportation fuels or as the basis for the synthesis of other chemicals. The ASPEN Plus™ process specifications and the modeling approach of the fuel synthesis unit are described in the following paragraphs in detail. The comparison with the conventional technologies (typical methanol reactor in the first case and the ethanol synthesis based on the reverse water gas shift (rWGS) reaction in the second one) is made in terms of efficiency by performing the thermodynamic analysis and in terms of economic feasibility.

Process description

The concept for transportation fuels through CO_2 hydrogenation is shown in Fig. 1. Carbon dioxide is separated and purified from the flue gas of a power intensive industry such as power sector or cement plant. The required hydrogen for the CO_2 hydrogenation is derived from water electrolysis that is accomplished with electricity derived either from renewable energy sources or from the grid. The process configuration for the CO_2 transformation into fuels and the final product separation and purification depends on the product type (methanol or ethanol). Since the CO_2 hydrogenation is accomplished in high pressure (>40 bar) both the inlet gases should be compressed before they are delivered to the CO_2 Utilization Unit (CUU).

Feedstock gases

The input gases that are required for the alternative ethanol synthesis are carbon dioxide (CO_2) and hydrogen (H_2).

Pure CO_2 separated from combustion gases of a power plant or other intensive carbon emission industry (e.g. cement plant) is considered as the source for the required CO_2. A great development has been gained on each of the main CO_2 separation techniques, even though no concept has reached to a commercial level yet. Among the several CO_2 caption options, amine scrubbing (MEA), Calcium Looping (CaL) and oxyfuel technology are considered the most competitive and ready to apply technologies for the first generation of applications in industrial scale. The chemical absorption technique with amine scrubbing is the most mature technology with the highest Technology Readiness Level and has already been tested and implemented in large scale applications [17]. Therefore, it is selected for this study as the CO_2 capture technology. For the process analysis the specific heat demands for amine regeneration are set 4.17 MJ_{th}/kg_{CO2} and the electric power consumption 0.021 kWh/kg_{CO2} [18].

The water electrolysis is the selected method for pure H_2 production. In this process, water is split into O_2 and H_2 by means of electrical power. This option has the lowest efficiency (35–42%) and the highest H_2 production cost (for large scale 20–25 $\$/GJ_{H2}$) among the other technological options. However, it is considered as the best option for sustainable and non-fossil fuels oriented hydrogen production [19,20]. Alkaline (KOH) electrolysis is the best available since it is quite mature up to large scale H_2 production [21]. Moreover, it has been tested successfully for discontinuous operation, and its load can be altered easily by adapting the current density [22]. Therefore, KOH electrolysis is selected as the most suitable technique for the examined concept in this study. Similar to the CO_2 capture, the water electrolysis process is not modeled